Summer student project—Aug08

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Project description:

Chemical synthesis of copper acetate mono deuterate and growth of crystals. $Cu_2[CD_3COO]_4.2D_2O$

$2\ CD_3COOD + Cu(OH)_2 + D_2O \rightarrow Cu_2[CD_3COO]_4.2D_2O$

Synthesis outline CAMH

The aim of the project was to synthesise fully deuterated copper acetate monohydrate crystals. A fully deuterated sample is necessary for the neutron spectroscopy measurements, due to the neutron scattering properties of hydrogen. However due to the cost and availability of CD_3COOD and D_2O initial attempts at the synthesis were carried out with normal acetic acid and deionised water.

After several trials the adopted synthesis of $Cu_2[CH_3COO]_4.2H_2O$ is as follows:

- In 100 cm^3 distilled H_2O, 10 cm^3 100% acetic acid solution dissolved and stirred for 2 minutes with magnetic stirrer at room temperature.
- Add to this solution 6g of $Cu(OH)_2$ powder, recording exact mass.
- Stir on hot plate and heat until boiling. When nearly all the H_2O has evaporated then pour solution onto filter paper on a watchglass - if there is a lot of H_2O remaining then filter over a beaker. Extract from beaker using a glass rod as many copper acetate crystals from side of beaker and place onto filter paper. Leave filter paper on watchglass to dry overnight in a desiccator with a continuous nitrogen flow.
- Weigh powdered crystals, and obtain percentage yield of sample. (% purity of approx 85% obtained)

Seed crystal methodology

Numerous attempts were made to create a reproducible method that systematically guaranteed production of seed crystals. However the method outlined below only increases the chances of producing good seed crystals.

At room temperature 7.5g of $Cu_2[CH_3COO]_4.2H_2O$ can be dissolved in 100cm^3 of H_2O whereas at 60°C 10.7 g can be dissolved. Solutions of 100 cm^3 were made up. In order to increase the rate of crystallization the solutions were prepared at

60°C. A slight excess of copper acetate was added so as to ensure saturation. Allow 45 minutes of stirring to ensure complete saturation. Filter into three 30 cm^3 new small plastic beakers. Cover the top of the beaker, and transfer to glass boxes for crystal growth. Nitrogen flow was adjusted at 200 cm^3 per minute for each beaker. Remove beaker cover and using a pipette add a couple of drops of H_2O- this helps prevent small crystals being formed on the surface and along the beaker sides. Leave for several days and cultivate seed crystals when they have formed. If a beaker has not produced decent seed crystals then the solution and the small crystals formed can be used to make a new saturated solution for recrystallization.

Notes and observations

From various solutions the seed crystals were collected and different shapes were observed. There were several monoclinic crystals which all came from the same solution which had been used once before to grow seed crystals and failed. These solutions were collected together and a new saturated solution was made from this. The solution had been filtered twice.

According to Braybrook, Heywood and Karatzas [1] monoclinic crystals were obtained in the control solution with no propan-1-ol. In 10% propan-1-ol solution the crystals are more cubic in shape. These latter crystals were found predominantly in the solutions that had been filtered only once. Therefore filtering the solution twice appears to give monoclinic crystals and removes more impurities.

Synthesis outline CAMD

Whilst one might expect the synthesis of $Cu_2[CD_3COO]_4.2D_2O$ to be very similar to the synthesis of the non-deuterated acetate the reaction conditions are slightly different. The first attempt at the synthesis produced large amounts of magnetic impurities and it was noted that the solution contained an emulsion and was lighter in colour than the usual dark blue saturated copper acetate solution. This was thought to be due to incomplete reaction between the copper hydroxide and the acetic acid.

Mr $Cu(OH)_2$ 97.57 $gmol^{-1}$

Mr CD_3COOD 64.08 $gmol^{-1}$

Mr D_2O 20.03 $gmol^{-1}$

Mr $Cu_2[CD_3COO]_4.2D_2O$ 415.40 $gmol^{-1}$

density CD_3COOD 1.1370gcm^{-3}

6g $Cu(OH)_2$ -- 0.0615mol

0.1230 mol CD3COOD no xs, use 0.150mol acid--> mass 9.612g →8.50cm^3

- In 100 cm^3 D_2O, 4.25 cm^3 100% acetic-d3-acid-d solution dissolved. Carry this out in the inert box in a 250 cm^3 conical flask. Add to this solution 3g of $Cu(OH)_2$ powder, recording exact mass.

- In fume hood stir on hot plate, and heat until boiling. Insert a nitrogen flow into top of flask so as to minimize the possibility of the solution interacting with the atmosphere. When nearly all the D_2O has evaporated then pour solution onto filter paper-if there is a lot of D_2O remaining then filter over a beaker. Extract using a glass rod the maximum amount of copper acetate crystals and place onto filter paper. Place filter paper on watchglass and leave to dry overnight in a desiccator with a continuous nitrogen flow.

- Weigh powdered crystals, and obtain percentage yield of sample. (% purity of approx 85% obtained)

Twice the volume of D_2O was used for the synthesis of the deuterated copper acetate. This caused the solution when saturated to be the same colour as the non deuterated solution. The solubility of copper acetate in D_2O was found to be less than in H_2O. At 20°C 5.5 g of copper acetate crystals dissolved in 100cm^3 D_2O and at 60°C the solubility was found to be 6.9g. The crystals produced from this batch were very small and crystallized very quickly, so the solutions were collected together and reused. To a batch of the initial deuterated product extra acetic acid was added, 1.5 cm^3 for 40 cm^3 of solution and then boiled to obtain the dry crystals. A sample was tested in the SQUID magnetometer and approx 1.4 g dissolved in D_2O to make saturated solution first at 20°C then more added at 60°C. The solution was placed in glass box and left to crystallize.

Julabo temperature regulators

Two Julabo water baths and a cooler were installed in the hope of increasing reliability of crystal growth. Several temperature gradients and locations of crystals were tried but no conclusive ideal setup was determined. On 21.08.08 a seed crystal was glued onto the end of a Pasteur pipette and placed halfway in glass vessel. Its original mass was 0.1120 g and its *a* and *b*-axes lengths are 11.29 and 4.73 mm respectively.

1) Braybrook AL, Heywood BR, Karatzas P. An experimental investigation of crystal/solvent interactions in the copper (II) acetate monohydrate/propan-1-ol system. Journal of Crystal Growth 244 (2002) 327-332.